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Absorption line CW EPR using an amplitude modulated longitudinal field

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Abstract

In standard continuous wave electron paramagnetic resonance (CW-EPR) experiments, the first derivative of absorption lines is detected. This type of a line shape is caused by the magnetic field modulation and is usually an undesired feature, since the sensitivity of CW-EPR drastically decreases with increasing linewidth. A new approach is introduced, which allows for the measurement of absorption line EPR spectra in systems with broad inhomogeneous lines. The method makes use of multiple-photon transitions that are induced in spin systems when a transverse microwave and a longitudinal radio frequency field are simultaneously applied. The absorption lines are obtained by using amplitude modulation of the radio frequency field and slight saturation of the spectral lines. The basics of the new approach are discussed and experimental examples are given.

Keywords: Electron paramagnetic resonance; EPR; ESR; Modulation; Absorption line shapes; Multiple photon transitions

1. Introduction

In electron paramagnetic resonance (EPR), modulation of the magnetic field followed by phase-sensitive detection is routinely used to increase the sensitivity of continuous wave (CW) EPR experiments [1]. As a result of the field modulation, derivative-like line shapes rather than absorption lines are recorded. A quantum-mechanical interpretation of CW-EPR proposed recently, provides for a deeper insight into the physical process behind this experiment [2]. It was shown, that the EPR lines are formed by multiple-photon transitions induced by a transverse microwave (mw) and a longitudinal radio frequency (rf) field.

The detection of EPR spectra with derivative-like line shapes has several disadvantages. The major disadvantage is that sensitivity drops rapidly for samples with broad EPR lines [1]. This is because the EPR signal intensity changes only slightly as a function of the magnetic field, so that field modulation does not significantly alter the detected signal. Thus large modulation amplitudes have to be used, which may cause distortions of the baseline and are usually limited to about 4 mT. A minor disadvantage is the more complex interpretation of the spectra and their comparison to absorption spectra obtained with other techniques. In principle, this can be remedied by integrating the spectrum, which is expected to result in the pure absorption spectrum. However, for weak signals the obtained absorption spectrum suffers strongly from baseline distortions and is thus not reproduced reliably. In addition, for modulation amplitudes comparable to or larger than the linewidth, contributions of higher-order sidebands are no longer negligible (modulation

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